

PATENT ABSTRACTS OF JAPAN

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(54) NON-AQUEOUS ELECTROLYTE AND NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the life of a battery by using an electrolyte composed of a non-aqueous solvent and lithium salt, and having a leakage current value below a specific value per a specific amount of natural graphite.

SOLUTION: A non-aqueous electrolyte is composed of a non-aqueous solvent and lithium salt and has a leakage current value of below 0.25 μ A per natural graphite of 1 mg. The non-aqueous electrolyte of 3 g to natural graphite of 1 g is allowed to exist in an electrochemical element composed of an electrode including natural graphite as an active material, and another electrode including metallic lithium as an active material, voltage of 0.01 V is applied thereto at 60°C, and current flowing after 25 hours from the start of the application of voltage is measured as a leakage current value preferably. The non-aqueous solvent is preferably composed of 95-99.99 wt.% of cyclic carbonic ester and/or chained carbonic ester, and 0.01-5 wt.% of a compound capable of being hardly soluble in the electrolyte when it is electrochemically decomposed. A non-aqueous secondary battery consists of a negative electrode composed of a carbon material capable of doping and dedoping a lithium ion, a positive electrode and the non-aqueous electrolyte.

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CLAIMS

[Claim(s)]

[Claim 1] It is nonaqueous electrolyte which is nonaqueous electrolyte containing a non-aqueous solvent and lithium salt, and is characterized by the leakage current value asked for the nonaqueous electrolyte by the following measuring method being below 0.25microper 1mg of natural graphites A.

3g is made for nonaqueous electrolyte to intervene to 1g of natural graphites in the electrochemistry component which consists of an electrode which uses a [measuring method of leakage current value] natural graphite as an active material, and an electrode of another side which uses a metal lithium as an active material, 0.01V are impressed to this component at 60 degrees C, the current value which flows 25 hours after electrical-potential-difference impression initiation is measured, and it considers as a leakage current value.

[Claim 2] Nonaqueous electrolyte according to claim 1 to which the aforementioned non-aqueous solvent is characterized by consisting of a compound which becomes at poor solubility at the electrolytic solution when electrochemically decomposed with an annular carbonate and/or a chain-like carbonate.

[Claim 3] Nonaqueous electrolyte according to claim 1 or 2 to which it is characterized by consisting of 0.01 - 5 % of the weight of compounds which become poor solubility at the electrolytic solution when the aforementioned non-aqueous solvent is electrochemically decomposed with an annular carbonate and/or 95 - 99.99 % of the weight of chain-like carbonates.

[Claim 4] Nonaqueous electrolyte according to claim 2 or 3 characterized by being at least one sort of compounds with which the compound which becomes poor solubility was chosen as the electrolytic solution from the group to which it consists of divinyl ethylene carbonate, vinyl ethylene carbonate, a maleic anhydride, phthalic anhydride, a FENI range (methyl carbonate), a divinyl sulfone, isocyanuric acid TORIKARUBOKISHI ethyl, and isocyanuric acid Tori (AKURIRO yloxy ethyl) when decomposed into the aforementioned electrochemistry target.

[Claim 5] The nonaqueous electrolyte rechargeable battery characterized by including the negative electrode which consists a lithium ion of doping and a carbon material which can carry out undoping, a positive electrode, and said nonaqueous electrolyte according to claim 1 to 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rechargeable battery using the nonaqueous electrolyte and it which raised the battery life in the detail more about nonaqueous electrolyte and a nonaqueous electrolyte rechargeable battery.

[0002]

[Background of the Invention] The cell using nonaqueous electrolyte has a high voltage and a high energy consistency, and since dependability, such as keeping, is high, it is widely used as a power source of consumer electronics. Typical existence of the rechargeable battery which used such nonaqueous electrolyte especially is a rechargeable lithium-ion battery.

[0003] As the electrolytic solution used for the rechargeable lithium-ion battery, the carbonate compound which has high dielectric constants, such as propylene carbonate and ethylene carbonate, is used as a solvent, or it considers as a mixed solvent with hypoviscosity carbonate compounds, such as diethyl carbonate, and the solution which dissolved electrolytes, such as LiBF_4 , LiPF_6 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , and Li_2SiF_6 , in it is used abundantly.

[0004] Moreover, as a negative electrode of a rechargeable lithium-ion battery, the occlusion of a lithium and the carbon material which can be emitted are mainly used, and is specifically classified into the graphite carbon material and the amorphous carbon ingredient. The spacing of the (002) field of a graphite carbon material is a high crystallinity ingredient 0.34nm or less, and an amorphous carbon ingredient is an ingredient with which the spacing of a field (002) exceeds 0.34nm. Since the lithium ion battery which used the graphite carbon material has large specific gravity with a small change of charge and discharge voltage, it has an advantage, like the discharge capacity per volume is large, and the lithium ion battery which used the amorphous carbon ingredient on the other hand has the advantage of excelling in the charge-and-discharge cycle property that the discharge capacity per weight is large.

[0005] By the cell which used such the electrolytic solution and a negative electrode, the reductive cleavage of a solvent tends to start at the time of first time charge, and the charge-and-discharge effectiveness at that time tends to fall. If high crystallinity carbon materials, such as a graphite, are used for a negative electrode and propylene carbonate and butylene carbonate are especially used as a non-aqueous solvent, the reductive cleavage of a solvent may occur violently at the time of charge, and the insertion reaction to the graphite of a lithium ion may hardly advance.

[0006] For this reason, although it is a solid-state in ordinary temperature as a non-aqueous solvent, the ethylene carbonate in which reductive cleavage cannot occur easily continuously is mixed to propylene carbonate, or the formula of restricting the content of the propylene carbonate in the electrolytic solution is taken. The reductive cleavage of a non-aqueous solvent was suppressed by it, and amelioration of the charge-and-discharge effectiveness at the time of first time charge and discharge has been achieved. However,

the cure is demanded also from the fall of a battery life which is easy to take place when elevated-temperature preservation and a charge-and-discharge cycle are repeated and which is considered to originate in very small reductive cleavage.

[0007] The method of adding various kinds of additives to an electrolyte as an approach of raising the elevated-temperature preservation property and charge-and-discharge cycle property of a cell is proposed. Generally, since the charge-and-discharge reacting weight to the electrode which stands in a row and happens to a electrolysis reaction and coincidence to the electrolysis reacting weight of the electrolytic solution on an electrode being very very small is very large, the decomposition current by the electrolysis reaction is buried in the charge-and-discharge reaction current, and cannot measure the very small electrolysis reaction on an electrode correctly by the usual approaches, such as cyclic voltammetry which evaluates electrochemical stability. Therefore, the present condition is whether the very small electrolysis reaction on an electrode is controlled in what kind of operation, and the elevated-temperature preservation property and charge-and-discharge cycle property of a cell are raised, and that what kind of no additives are still known.

[0008]

[Problem(s) to be Solved by the Invention] Then, this invention aims at offering the nonaqueous electrolyte which improved the elevated-temperature preservation property of a cell etc., and offer of the rechargeable battery which raised the battery life using the nonaqueous electrolyte.

[0009]

[Means for Solving the Problem] That is, this invention is nonaqueous electrolyte containing a non-aqueous solvent and lithium salt, and the nonaqueous electrolyte is related with the nonaqueous electrolyte whose leakage current value calculated by the following measuring method is below 0.25microper 1mg of natural graphites A.

[0010] 3g is made for nonaqueous electrolyte to intervene to 1g of natural graphites in the electrochemistry component which consists of an electrode which uses a [measuring method of leakage current value] natural graphite as an active material, and an electrode of another side which uses a metal lithium as an active material, 0.01V are impressed to this component at 60 degrees C, and the current value which flows 25 hours after electrical-potential-difference impression initiation is measured, and let that value be a leakage current value.

[0011] As the aforementioned non-aqueous solvent, when [like an annular carbonate and/or a chain-like carbonate divinyl ethylene carbonate and vinyl ethylene carbonate, a maleic anhydride, phthalic anhydride, a FENI range (methyl carbonate), a divinyl sulfone isocyanuric acid TORIKARUBOKISHI ethyl and isocyanuric acid Tori (AKURIRO yloxy ethyl)] decomposed electrochemically, it is desirable that compounds which become poor solubility are consisted of by the electrolytic solution. Moreover, as lithium salt which dissolves in the electrolytic solution, LiPF₆ and LiBF₄ grade are desirable and the concentration has the desirable range of 0.1-3 (a mol/l).

[0012] Moreover, this invention relates to the nonaqueous electrolyte rechargeable battery containing the negative electrode which consists a lithium ion of doping and a carbon material which can carry out undoping, a positive electrode, and the aforementioned nonaqueous electrolyte.

[0013]

[Detailed Description of the Invention] Next, each configuration of the rechargeable battery using the nonaqueous electrolyte and it concerning this invention is explained concretely.

[0014] ** Water ** Solution The nonaqueous electrolyte concerning liquid this invention is the electrolytic solution containing a non-aqueous solvent and the lithium salt as an electrolyte, and it is desirable for the leakage current value observed when it measures by the approach of mentioning this nonaqueous electrolyte later to be below 0.1microA more preferably below 0.20microA below 0.25microper 1mg of natural graphites A.

[0015] Although the current which flows when a fixed electrical potential difference is impressed to the electrochemistry component which consists of a positive electrode, a negative electrode, and nonaqueous electrolyte is divided roughly into the current consumed by the charge-and-discharge reaction of an electrochemistry component, and the current consumed by electrolysis of the non-aqueous solvent on an electrode, if time amount which continues impressing a fixed electrical potential difference to an electrochemistry component is lengthened, the current value consumed by charge and discharge will become small gradually, and will approach 0 in approximation. Therefore, the current value measured after continuing impressing fixed time amount and a fixed electrical potential difference is mostly equivalent to the current value consumed by electrolysis of the non-aqueous solvent on an electrode.

[0016] Therefore, the above mentioned current value is a value when the charge and discharge current in the inside of a cell approaches 0 in approximation, the excessive side reaction which decomposition of the non-aqueous solvent in the inside of a cell is controlled as the current value is less than [0.25microA/mg], and has a bad influence on a cell property cannot occur easily, and has become, as a result, an elevated-temperature preservation property, a charge-and-discharge cycle property, etc. of a cell are improved, and its battery life improves. So, such nonaqueous electrolyte is suitable as the electrolytic solution for a primary cell and rechargeable batteries. On these specifications, this current value is henceforth called a "leakage current value."

[0017] A leakage current value is measured using the equipment described below. That is, while constitutes an electrochemistry component and the electrode which uses a natural graphite as an active material is prepared as an electrode. As a natural graphite, China-Vietnam graphite factory trade name LF-18A can be used, for example, and the amount of natural graphites is set to 15mg or more, and the amount of superintendent officers of an electrode is made into about two 10 - 15 mg/cm. In addition, that to which the natural graphite to be used performed surface treatment is not suitable, and it is not appropriate to carry out a reuse from what, and repeated 20 or more cycle charge-and-discharge actuation, or performed the elevated-temperature preservation test, either. [what] [carrying out the mothball for two weeks or more as an electrochemistry cel]

[0018] As another electrode, the electrode which uses a metal lithium as an active material is prepared. If the porous film of the electric insulation into which nonaqueous electrolyte was infiltrated is made to intervene between two electrodes, the electrochemistry component for measurement will be done. LiPF6 which is an electrolyte at nonaqueous electrolyte -- a non-aqueous solvent -- 0.5-2 -- it is dissolving by the concentration of 0.7-1.5 (a mol/l) preferably. Here, let the weight ratio of an electrode and nonaqueous electrolyte be nonaqueous electrolyte 2-4 to a natural graphite 1.

[0019] Thus, after aging beforehand for the manufactured electrochemistry component,

0.01V are impressed at 60 degrees C, and impression is continued for it for 25 hours. As that example was shown in drawing 3, the current value which flows for this electrochemistry component with impression, i.e., a leakage current value, decreases gradually, and if 15 hours is exceeded, it will turn into about 1 constant value. Therefore, measurement of the leakage current impresses 0.01V at 60 degrees C, calculates the measured value 25 hours after impression initiation, converts the measured value (muA) into the value per 1mg of natural graphites, and makes the reduced property a leakage current value (muA/mg).

[0020] The nonaqueous electrolyte concerning configuration this invention of nonaqueous electrolyte dissolves lithium salt in a non-aqueous solvent, it is the electrolytic solution on which it acts as an electrolyte, and, as for the nonaqueous electrolyte used, the above-mentioned leakage current value is measured below at 0.25micropor 1mg of natural graphites A.

[0021] As lithium salt usable as an electrolyte, lithium salt, such as LiF, LiCl, LiBr, LiI, Li2SO4, LiOH, LiSO3CH3, LiSO3C6H4CH3, LiPF6, LiBF4, LiClO4 and LiAsF6, Li2SiF6, LiC4F9SO3, and LiC8F17SO3, is mentioned.

[0022] Moreover, the lithium salt shown by the following general formula can also be used. LiOSO two R8, LiN (SO two R9) (SO two R10), LiC (SO two R11) (SO two R12) (SO two R13), LiN (SO2OR14) (SO2OR15) (here, even if R8-R15 are mutually the same, they may differ from each other, and they are the perfluoroalkyl radical of carbon numbers 1-6). These lithium salt may be used independently, and it may use it, combining two or more sorts and mixing it.

[0023] Among these, LiPF6, LiBF4, LiOSO two R8, and LiN (SO two R9) (SO two R10), LiC (SO two R11) (SO two R12) (SO two R13) and LiN (SO2OR14) (SO2OR15) are desirable, and LiPF6 and LiBF4 are used further most preferably.

[0024] As a non-aqueous solvent, they are others [carbonate]. Methyl formate, ethyl formate, Propyl formate, methyl acetate, ethyl acetate, propyl acetate, methyl propionate, Chain-like carboxylate, such as ethyl propionate Phosphoric ester, such as trimethyl phosphate, The chain-like ether, such as dimethoxyethane Cyclic ether, such as a tetrahydrofuran, Amides, such as dimethylformamide Chain-like carver mates, such as methyl-N and N-dimethyl carver mate, Cyclic ester, such as gamma-butyrolactone Annular sulfones, such as a sulfolane, Annular carver mates, such as N-methyl oxazolidinone Cyclic amide, such as N-methyl pyrrolidone Solvents, such as annular urea, such as N and N-dimethyl imidazolidone, and such mixture can be used.

[0025] Also in these non-aqueous solvents, a point to the carbonate or chain-like carboxylate of electrochemical stability is desirable, and it is still more desirable that they are an annular carbonate and a chain-like carbonate. As an example of an annular carbonate, ethylene carbonate, propylene carbonate, 1, 2-butylene carbonate, 2, 3-butylene carbonate, 1, 2-pentene carbonate, 2, and 3-pentene carbonate etc. is mentioned. As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned.

[0026] both are mixed and used for an annular carbonate and a chain-like carbonate -- desirable -- the mixed rate at that time -- weight % -- expressing -- an annular carbonate:chain-like carbonate -- 5:95-95:5 -- it is 20:80-60:40 preferably.

[0027] Moreover, to the nonaqueous electrolyte concerning this invention, it is desirable

to mix a small amount of additive of fusibility to a solvent in addition to the aforementioned non-aqueous solvent. As such an additive, when decomposed electrochemically, it is the compound which becomes poor solubility to the electrolytic solution, for example, the compound which has two or more reacting points in intramolecular can be suitably used like the unsaturated compound which has a multiple bond like a carbon-carbon double bond, and isocyanuric acid ester.

[0028] The following compound can be mentioned as an example.

(a) An unsaturated compound like divinyl ethylene carbonate, vinyl ethylene carbonate, AKURIRO xyloxy methyl ethylene carbonate, METAKURIRO xyloxy methyl ethylene carbonate, the partial saturation carbonate compound (b) maleic acid that has a double bond like a FENI range (methyl carbonate), a maleic anhydride, N-ethyl maleimide, a phthalic acid, phthalic anhydride, SURUHOREN, and a divinyl sulfone [0029] (c) Isocyanuric acid TORIKARUBOKISHI ethyl, isocyanuric acid Tori (methoxy carbonylethyl), isocyanuric acid Tori (ethoxy carbonylethyl) and isocyanuric acid trialkyl (alkyl group: -- methyl --) Ethyl, propyl, isocyanuric acid Tori (trimethoxysilylpropyl), isocyanuric acid Tori (hydroxyethyl), isocyanuric acid Tori (glycidyl), isocyanuric acid Tori (AKURIRO xyloxy ethyl), isocyanuric acid Tori (meta-KURIRO xyloxy ethyl), isocyanuric acid TORIBINIRU, an isocyanuric acid triaryl, and the isocyanuric acid ester [0030] like isocyanuric acid triphenyl Also in these, divinyl ethylene carbonate, vinyl ethylene carbonate, a maleic anhydride, phthalic anhydride, a FENI range (methyl carbonate), a divinyl sulfone, isocyanuric acid TORIKARUBOKISHI ethyl, and isocyanuric acid Tori (AKURIRO xyloxy ethyl) are desirable.

[0031] As for these additives, it is desirable to carry out addition mixing so that it may become the rate of 95 - 99.99 % of the weight of non-aqueous solvents and 0.01 - 5 % of the weight of additives into nonaqueous electrolyte. If it is within the limits of this, the effectiveness of decreasing a leakage current value can appear and the elevated-temperature preservation property and charge-and-discharge cycle of a cell can be raised.

[0032] the lithium salt as an electrolyte is dissolved into the non-aqueous solvent containing the aforementioned additive -- having -- 0.1-3 (a mol/liter) -- preferably, it is prepared by the density range of 0.5-2 (a mol/liter), and is used for it. Additives, such as a stabilizer, can be suitably added to nonaqueous electrolyte if needed.

[0033] Whether it is desirable when using it in the state of the solution which dissolved lithium salt in the non-aqueous solvent makes lithium ion conductivity high, and it uses the solution in the condition of having sunk into the porous insolubility macromolecule or it uses the nonaqueous electrolyte explained until now in the state of the gel polyelectrolyte made to swell a high polymer with the electrolytic solution, it may be used in the condition of having sunk into inorganic support, such as an alumina and a silica, further.

[0034] 2 [s] degree ** The rechargeable battery concerning pond this invention consists of a negative electrode containing the carbon material in which the dope of a lithium ion and a dedope are possible as a negative-electrode active material, a positive electrode, and above-mentioned nonaqueous electrolyte.

[0035] As a negative-electrode active material, the carbon material in which the dope of a lithium ion and a dedope are possible is used, and it divides roughly as a carbon material desirable in it, and is classified into a graphite carbon material and an amorphous carbon ingredient. A graphite carbon material is an ingredient with which the spacing of the

(002) field consists of crystalline high carbon 0.34nm or less, and an amorphous carbon ingredient is an ingredient with which the spacing of a field (002) exceeds 0.34nm. When a graphite carbon material is used especially, the effectiveness of decreasing the leakage current is high and, specifically, what calcinated the substrate containing a natural graphite, a mesophase carbon fiber, a mesophase carbon micro bead, and other various carbon above 2000 degrees C, pyrolytic graphite, etc. are mentioned.

[0036] Moreover, as positive active material which constitutes a positive electrode, the multiple oxide, LiCoO_2 and LiMnO_2 , which consists of a lithium and transition metals, LiMn_2O_4 , LiNiO_2 , $\text{LiNiCo}(\text{1-X})\text{O}_2$ or a transition-metals oxide and a sulfide 2, for example, MoS , V_2O_5 , TiO_2 and MnO_2 , or a conductive polymer, for example, a poly aniline-disulfide compound, can be used. [for example,] The multiple oxide which especially consists of a lithium and transition metals is desirable.

[0037] The nonaqueous electrolyte rechargeable battery using such an ingredient can be fabricated and used for configurations, such as cylindrical, a coin mold, a sheet mold, or a square shape. A cylindrical nonaqueous electrolyte rechargeable battery is explained as an example of representation. As that structure is shown in drawing 1, this cell is contained with the cell can 5 through the separator 3 with which the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, and becomes it, and the positive electrode 2 which comes to apply positive active material to the positive-electrode charge collector 10 were poured into nonaqueous electrolyte, where [of winding and this winding object] an electric insulating plate 4 is laid up and down. the cell can 5 -- the cell lid 7 -- the ** ROGASU blanket 6 -- minding - - by closing, it is attached, connects with a negative electrode 1 or a positive electrode 2 electrically through the negative-electrode lead 11 and the positive-electrode lead 12, respectively, and is functioning as the negative electrode or positive electrode of a cell.

[0038] In drawing 1, although the porous film is used as a separator 3, and the case of the gel polyelectrolyte made to swell a high polymer in nonaqueous electrolyte and nonaqueous electrolyte were infiltrated into inorganic support, such as an alumina and a silica, as an electrolyte, a separator is not necessarily required for a case.

[0039] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 is planned through the sheet metal 8 for current cutoff. When the pressure inside a cell rises, the sheet metal 8 for current cutoff is pushed up, and deforms, the positive-electrode lead 12 leaves the above-mentioned sheet metal 8 and the welded part, and is cut, and it is that a current is intercepted as like.

[0040] Drawing 2 is the example of a coin mold nonaqueous electrolyte rechargeable battery. By this cell, the laminating of the disc-like negative electrode 13, the disc-like positive electrode 14, the separator 15 containing nonaqueous electrolyte, aluminum or the stainless plate 17, and the spring 20 is carried out in a negative electrode 13, a separator 15, a positive electrode 14, aluminum or the stainless plate 17, and the sequence of a spring 20. each part article is contained with the cell can 16 in the state of this laminating -- having -- the cell can top 19 -- a gasket 18 -- minding -- it is attached by closing. The same thing as the above is used as a negative electrode 13, a separator 15, and a positive electrode 14. Moreover, the thing of the quality of the material of the stainless steel by which the cell can 16, the cell can top 19, and a spring 20 cannot be easily corroded with the electrolytic solution is used.

[0041]

[Example] Next, although this invention is concretely explained through an example, this invention is not limited at all by these examples.

[0042] First, the natural-graphite electrode and LiCoO₂ electrode were produced, Li-natural-graphite cell and the LiCoO₂-natural-graphite cell were produced using it, it was attached to each cell, and the leakage current value and the elevated-temperature preservation property were measured.

[0043] as a <production of natural-graphite electrode> graphite carbon material, a natural graphite (a China-Vietnam graphite company product, LF-18A) is prepared, this natural-graphite powder 87 weight section and the polyvinylidene fluoride (PVDF) 13 weight section of a binder are mixed, and it distributes to N-methyl pyrrolidinone of a solvent -- making -- a natural graphite -- a mixture -- the slurry was prepared. this negative electrode -- a mixture -- after making the charge collector with a thickness of 18 micrometers made from band-like copper foil apply and dry a slurry, it pressed, this was pierced to discoid with a diameter of 14mm, and the coin-like natural-graphite electrode was obtained. this natural-graphite electrode -- the thickness of a mixture was 110 micrometers and weight was 14mm of 20 mg/phi.

[0044] the <production of LiCoO₂ electrode> LiCoO₂ (Honjo FMC energy systems company product, HLC-21) 90 weight section, the graphite 6 weight section as electric conduction material, the acetylene black 1 weight section, and the polyvinylidene fluoride (PVDF) 3 weight section as a binder are mixed, and it distributes to N-methyl pyrrolidinone of a solvent -- making -- LiCoO -- the slurry was prepared 2 mixture, this LiCoO -- after making aluminum foil with a thickness of 20 micrometers apply and dry a slurry 2 mixture, it pressed, this was pierced to discoid with a diameter of 13mm, and LiCoO₂ electrode was produced. The thickness of LiCoO₂ mixture was 90 micrometers and weight was 13mm of 35 mg/phi.

[0045] The coin mold cell shown in <production of Li-natural-graphite cell> drawing 2 was produced. That is, the laminating of the separator 15 with 25 micrometers [in the metal lithium foil 13 with a thickness of 0.3mm and thickness] and a diameter of 19mm made from a fine porosity polypropylene film was carried out to the cell can 16 of 2032 sizes made from stainless steel at the sequence of the metal lithium foil 13, a separator 15, and the natural-graphite electrode 14 for the natural-graphite electrode 14 with a diameter of 14mm and the diameter of 16mm.

[0046] Then, 0.05ml of nonaqueous electrolyte was poured into the separator 15, and the plate 17 of further the product made from stainless steel with 1.5mm [in thickness] and a diameter of 15.5mm and the spring 20 were contained with the cell can 16. By closing the cell can top 19 at the last through the gasket 18 made from polypropylene, the airtightness in a cell was held and the coin mold Li-natural-graphite cell with a diameter [of 20mm] and a height of 3.2mm was produced.

[0047] The laminating of the separator 15 with 25 micrometers [in LiCoO₂ electrode / 14 / of with a <production of LiCoO₂-natural-graphite cell> diameter of 13mm, the natural-graphite electrode 13 with a diameter of 14mm, and thickness] and a diameter of 16mm made from a fine porosity polypropylene film was carried out to the cell can 16 of 2032 sizes made from stainless steel at the sequence of the natural-graphite electrode 13, a separator 15, and LiCoO₂ electrode 14.

[0048] Then, 0.03ml of nonaqueous electrolyte was poured into the separator 15, and the plate 17 of further the product made from aluminum with 1.2mm [in thickness] and a

diameter of 16mm and the spring 20 were contained with the cell can 16. By closing the cell can top 19 at the last through the gasket 18 made from polypropylene, the airtightness in a cell was held and the coin mold LiCoO₂-natural-graphite cell with a diameter [of 20mm] and a height of 3.2mm was produced.

[0049] In advance of leakage current value measurement of a <measurement of leakage current value> Li-natural-graphite cell, it aged on the conditions described below. After aging conditions discharge to 0V with the current density of about 0.6 mA/cm², they are held to 0V, make all charging time values 10 hours, after charging to 1.2V with the current density of about 0.6 mA/cm² after that, are held to 1.2V and make all the charging times 10 hours. Next, only this actuation is two-cycle ***** , using [after about 1.2mA /discharges to 0V with the current density of 2 cm, it holds to 0V and make all charging time values into 5 hours and] as 1 cycle charge-and-discharge actuation which holds to 1.2V and makes all the charging times 5 hours, after about 1.2mA /charges to 1.2V with the current density of 2 cm after that.

[0050] Next, the temperature up of this cell was carried out to 60 degrees C, all 25-hour discharge was continued on condition that 0.2mA constant current and 0.01V constant voltage, the current value which flowed on the cell at this time was measured, and the current value change to a charging time value was pursued. The current value of 25 hours after was measured for leakage current value count.

[0051] In the case of the <elevated-temperature preservation test> Li-natural-graphite cell, it aged on the same conditions as the above first, and discharge of a total of 10 hours was carried out to it as a 3 cycle eye of a part after that and the second half on condition that 2mA constant current and 0.01V constant voltage. Subsequently, after saving this cell for 14 days at a 60-degree C thermostat, charge of a total of 5 hours was performed on condition that 2mA constant current and 1.2V constant voltage. At this time, it asked for the ratio of the charge capacity after the preservation to the discharge capacity of 3 cycle eye before elevated-temperature preservation as a capacity survival rate (%). The elevated-temperature preservation property was evaluated based on this capacity survival rate.

[0052] In the case of the LiCoO₂-natural-graphite cell, it aged the following condition first. That is, on condition that 0.5mA constant current and the constant voltage of 4.2V, it charged until the current value of 4.2V was set to 0.05mA, and after that, on condition that 1mA constant current and the constant voltage of 3.0V, it discharged until the current value of 3.0V was set to 0.05mA. Subsequently, on condition that 1mA constant current and the constant voltage of 3.85V, it charged until the current value of 3.85V was set to 0.05mA.

[0053] Subsequently, it saved for one day at the 60-degree C thermostat, and after that, on condition that 1mA constant current and the constant voltage of 3.0V, it discharged until the current value of 3.0V was set to 0.05mA. It asked for the ratio of the discharge capacity after preservation to the charge capacity to 3.85V as a capacity survival rate (%) before the elevated-temperature preservation at this time.

[0054] (Example 1) 15.2g (100mmol) is dissolved in the mixed solvent of ethylene carbonate (EC, 39.8 % of the weight), dimethyl carbonate (DMC, 59.7 % of the weight), and divinyl ethylene carbonate (DVEC, 0.5 % of the weight), LiPF₆ is set to 100ml at 25 degrees C, and it is LiPF₆ concentration. The nonaqueous electrolyte of 1 (mol/l) was prepared.

[0055] The leakage current value was measured about this nonaqueous electrolyte. as drawing 3 showed, the current which flowed on Li-natural-graphite cell, i.e., the leakage current, became about 1 law in 15 - 25 hours, and the leakage current value of 25 hours after was 0.22microA per 1mg of natural graphites. Moreover, the elevated-temperature preservation property of Li-natural-graphite cell was investigated, and the capacity survival rate (%) was indicated to Table 1.

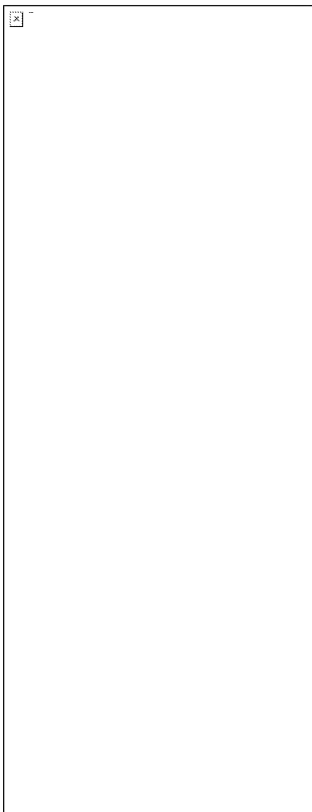
[0056] (Example 2) In the example 1, except having changed the mixed rate of ethylene carbonate (EC), dimethyl carbonate (DMC), and divinyl ethylene carbonate (DVEC), it was operated like the example 1 and the leakage current value was measured. Moreover, the capacity survival rate (%) was measured, and this nonaqueous electrolyte was applied to the LiCoO₂-natural-graphite cell, and it described in Table 1 collectively.

[0057] (Examples 3-10) In the example 1, it carried out like the example 1 except having used vinyl ethylene carbonate, a maleic anhydride, phthalic anhydride, a FENI range (methyl carbonate), isocyanuric acid TORIKARUBOKISHI ethyl, isocyanuric acid Tori (AKURIRO yloxy ethyl), and a divinyl sulfone instead of divinyl ethylene carbonate, respectively. The result of having measured the leakage current value was described in Table 1.

[0058] (Example 1 of a comparison) As nonaqueous electrolyte, except having used the mixed solvent of ethylene carbonate (EC, 40 % of the weight) and dimethyl carbonate (DMC, 60 % of the weight), it carried out like the example 1, the leakage current value was measured, and it indicated collectively to Table 1. Furthermore, it measured also about the capacity survival rate (%) of Li-natural-graphite cell and a LiCoO₂-natural-graphite cell, and described in Table 1.

[0059]

[Table 1]



[0060] The capacity survival rate in an elevated-temperature retention test was also so

high that the leakage current value became small, and the result of examples 1-10 and the example 1 of a comparison showed that a battery life improved.

[0061]

[Effect of the Invention] Since the nonaqueous electrolyte of this invention made the leakage current value below 0.25microper 1mg of natural graphites A, it can control the electrolysis reaction of the non-aqueous solvent on an electrode to the minimum, and is stable nonaqueous electrolyte. Furthermore, the elevated-temperature preservation property of the rechargeable battery which used such nonaqueous electrolyte is improving, and it is thought that it contributes to amelioration of a charge-and-discharge cycle property and extension of a battery life.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the cylindrical rechargeable battery which applied the nonaqueous electrolyte concerning this invention.

[Drawing 2] It is the sectional view of the coin mold rechargeable battery which applied the nonaqueous electrolyte concerning this invention.

[Drawing 3] It is the chart which shows change of the leakage current value (μA) which flowed on the cell to a charging time value (hr).

[Description of Notations]

1 13 Negative electrode

2 14 Positive electrode

3 15 Separator

5 16 Cell can

7 19 Cell lid

9 Negative-electrode charge collector

10 Positive-electrode charge collector
